Reactive imbibition of WC-Co substrate for PDC cutters used in oil and gas and mining drilling

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Reactive Imbibition of WC-Co Substrate for PDC Cutters Used in Oil and Gas and Mining Drilling

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Abstract

Cemented carbides are used in rock drilling for mining tools and wear resistant parts. These composite materials possess an excellent compromise between hardness and toughness. Nowadays, the concept of graded structure is widely studied to improve these two properties simultaneously, and so to increase the service life of drilling tools.

A continuous composition gradient on several millimetres is generated in commercial WC-Co substrate for PDC cutters by using Reactive Imbibition method. The effects of this process are analysed in terms of microhardness, cobalt concentration and WC grain size. A continuous gradient of about 300HV on 8mm-height substrate is obtained in one-step by imbibition process into combination with a boron-rich coating deposed on its free surface. In part, this gradient of hardness and its shape are preserved after HPHT (high pressure-high temperature) process that is used for the diamond table deposition on the WC-Co substrate. Such gradient must significantly increase the cutter service life.

Keywords: Cemented Carbides, Functionally Graded Materials (FGM), Imbibition

Introduction

The goal of this study is to develop a new process to enhance the service life of drilling tools cutters. Indeed, drilling conditions in deep and heterogeneous wells lead to premature wear and fracture of tools because of abrasive rocks and repeated shocks. Drilling tools are made of cemented carbides which are composed of WC hard phase embedded in a Co-based ductile metallic matrix.

In order to increase hardness and toughness, which are antagonistic properties, Functionally Graded Material (FGM) way is chosen. Gradation of cemented carbides is not a recent idea, its interest has been demonstrated in 1972 [1]. Since, a lot of processes have been developed to grade WC-Co: Infiltration [2], Dual Properties (DP) carbides [3], [4], [5], Carbide Free Layer (CFL) [6], [7], [8], [9], Ion implantation [10], Cr_3C_2 coating on cemented carbides before sintering [11] and multilayers or stacking of different cemented carbides by their cobalt content and carbide grain size [12], [17]. These processes rely on different techniques, which have two common drawbacks:

- the small distance on which is developed the cobalt redistribution,
- the discontinuity of gradients of the hardness and cobalt content.

But, there is another gradation process which overcomes these drawbacks: Imbibition from dense cemented carbides allows to continuously enrich the substrates in binder phase (between 10 and 20wt.% Co) over several millimetres (about 10 to 20mm). First results on this process were published in 1972 by Lisovsky and Babich [13].

Recently, Reactive Imbibition [14], patented by Varel Europe/Armines is a one step process combining imbibition from dense cemented carbides and a boron-rich coating on their free surfaces. This new process generates a continuous variation of cobalt through several millimetres and with an excellent gradient shape control to increase at the same time the surface hardness and core toughness.

In this article, this new process has been chosen to grade the substrate of commercial cutters. The underlying principles governing the cobalt phase migration and distribution are examined and based on thermodynamic properties and phase reactions during imbibition and HPHT treatments with the aim of gaining an understanding of the phenomena.

Reactive Imbibition process

A. Imbibition treatment

Imbibition consists in a migration of liquid arising from a reservoir (filler material) in a two-phase system (solid / liquid) which is raised to high temperature. This phenomenon is different from well-known diffusion mechanism, because the liquid migration has the same composition than liquid within sample. The imbibition phenomenon is also different from infiltration mechanism which implies a three-phase system (solid / liquid / gas, i.e. a porous media). According to Lisovsky [13], three conditions are required in a two-phase system to make imbibition possible: a good wetting of solid grains by the liquid matrix, a partial dissolution of solid grains in this liquid matrix and the absence of equilibrium dihedral angle defined by $\gamma_{SS}/2\gamma_{SL}>1$. So, if the ratio

of the solid-solid to solid-liquid surface energy is high (>2), then the penetration of grain boundaries by liquid is possible because it is energetically more favourable to system evolution. Also, in the process of imbibition, the liquid phase in contact with a fully dense cemented carbide flows through the liquid channels formed by refractory particles (WC grains). A complete reconstruction of the refractory skeleton by particle rearrangement occurs during migration and Park [15] deals with this phenomenon by determination of the minimum interface energy configurations of solid / liquid system with varying dihedral angles and liquid contents. A similar approach is undertaken by Delannay and al [23] that expresses the variation of driving force for the absorption of liquid by solid/liquid system as a function of the liquid volume fraction, U, and the coordination number, n_c. On the other hand, the Ostwald ripening with a modification of grain shape, without necessary grain growth is not a condition essential to liquid migration in imbibition process, according to Sorlier [14]. However, the driving force of liquid migration for the assemblies of fully dense cemented carbides is the reduction of the interfacial energy by the grain shape accommodation, according to Colin [16], [17]. The author puts forward the dwell time very long (several hours) used for these assemblies which allows the grain shape accommodation.

Usually, WC particles have an anisotropic solid / liquid interfacial energy. The system reaches its minimum energy for a certain amount of binder phase which allows adopting its equilibrium configuration, corresponding to lower energy level. Until the critical amount of binder phase has not been reached, a migration pressure exists in the system. The phenomenologic expression of the liquid migration pressure P_{mig} (MPa), established by Lisovsky is given by expression corrected by Sorlier [14]:

$$P_{mig} = \frac{0{,}848}{d_{WC}}\left[\left(\frac{1-U}{U}\right)^{1/3} - 1{,}41U\right]$$

where U is the volume fraction of liquid and d_{WC} (µm) is the mean WC grain size. It is thus predicted that the liquid migration pressure increases when the WC grain size and the Co content are smaller. This expression also points out that this migration pressure reaches zero for a critical volume fraction of liquid (U_m=*0.61*) which corresponds to 32 wt.% Co. Thus, a WC-Co containing more than 30 wt.% Co cannot be enriched in binder phase.

B. Reactive coating mechanism

A boron nitride coating is uniformly deposited on WC-Co part by spraying (Fig. 1a). Just before the migration of liquid from a reservoir composed of green part with eutectic composition, the BN coating is destabilized by liquid phase, after the solidus of the cemented carbide is reached. According the mechanism proposed by Sorlier [14], this destabilization leads to a diffusion of boron inside the substrate through its liquid phase (Fig. 1b). The solubility of boron into the liquid phase is small and so, its saturation is quickly reached. Also, borides, in particular WCoB, precipitate under the substrate surface. The formation of this ternary compound involves a decrease of W and Co contents into the liquid phase. So, the carbon in excess in the liquid can diffuse towards the bulk (Fig. 1c), causing the diffusion of the cobalt in the same direction, as for the DP carbides. Indeed, it is well-known that when there is a carbon gradient into the liquid, cobalt appears to migrate in the direction of carbon diffusion, resulting in a redistribution of cobalt in the cemented carbide [18]. However, the microstructure shows no free-carbon nor η-Co_3W_3C phase.

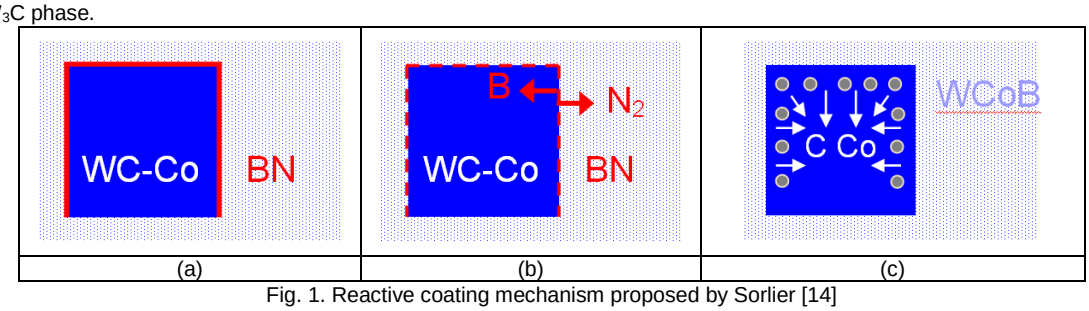


Fig. 1. Reactive coating mechanism proposed by Sorlier [14]

Experimentation

A. Materials and sample preparation

The WC-Co substrates used in this study are commercial ones. The cylinder-shape substrates for cutters have a 14.40mm diameter and a height ranging from 7.35 to 8.10mm. Their initial Co content is 12.25 wt.%, their grain size measured by linear intercept ranges from 0.5 to 4µm and they are fully dense (Porosity< 0.02% according to ASTM B276). The hardness of these substrates is measured under a 2kg load and reaches 1245 +/- 30 HV.

The green part composed of the eutectic composition (WC-65wt.% Co) is prepared with powders supplied by Ceratizit. Once the powders have been blended in a mixer for 24h, 10mm diameter compacts are cold pressed at 200MPa by uniaxial compaction. During this time, the commercial substrates are cleaned in an ultrasonic alcohol bath for 5min. Coating is applied to those which need it.

Once the green part and the substrate have been prepared, the BN-coated substrate is superimposed on the green part before being put in a graphite furnace. The sample is processed at 1450℃ under an Ar-5vol.% H_2 atmosphere in order to approximate industrial conditions. Then, the processed substrate has undergone a classic High Pressure / High Temperature (HPHT) step in order to assembly the diamond table on the WC-Co substrate. This treatment consisting in a quick heating of the substrate with diamond powder in a refractory metallic cap is carried out for a few minutes under a stable temperature / pressure condition adapted to diamond. In order to clarify the running of the experiment, Fig. 2 presents a schematic

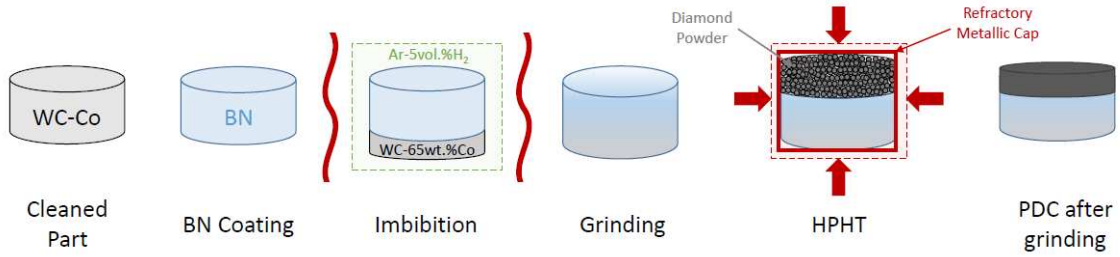


Fig. 2. Major steps of the process

representation of the major steps of the process.

After the reactive imbibition treatment or the HPHT process, depending on the sample, the cutters are electric-discharge machined in order to cut them into two equal parts, ready to be polished and analysed. The samples are then ground and polished to a 1µm finish for microstructural examinations.

The diamond tables are processed under two Pressure/Temperature combinations, with the second combination at higher Pressure/Temperature. Two grain size distributions are used for the diamond (coarse and fine). The table 1 summarizes processed samples.

Table 1. Summary of the samples

	WC-Co Cutters		HPHT Conditions	
	As-received	**Reactive Imbibition**	**Diamond**	**Pressure/Temperature**
A	X			
B		X		
C	X		Coarse	1
D		X	Coarse	1
E	X		Fine	1
F		X	Fine	1
G	X		Coarse	2
H		X	Coarse	2
I	X		Fine	2
J		X	Fine	2

B. Characterization of cutters

To characterize the microstructure, a Zeiss-DSM982 Scanning Electron Microscope (SEM) in secondary electron (SE) and back-scattered electron (BSE) modes under a 10 kV voltage is used. After microstructure binarization, linear intercept analysis is performed on nine SEM micrographie at x5000 magnification for each position. These nine micrographie are performed around hardness indentations in order to control the WC grain size along the revolution axis. This grain size measurement allows to verify that the two successive thermal treatments (imbibition and HPHT) have not generated normal and abnormal grain growth (Fig. 3.a).

In order to quantify the liquid migration in the sample, three experimental techniques based upon different principles have been compared. This first one is founded on the hardness measurement, since it is related to Co content for a constant grain size. A Buehler microhardness tester with a Vickers diamond tip is used to determine the Vickers hardness with a load of 2kg and an indentation time of 10s, according to NF A 03-154. Indentations are performed along the revolution axis and on the right part of the sample, because the Co migration is symmetrical across this axis. Three hardness measurements are performed for each pre-determined position. The second method to measure the Co content is based upon image analysis. For an isotropic microstructure, surface fraction is equivalent to volume fraction of each phase in a two-phase structure. Then, the volume fraction of cobalt (V_{Co}) is converted into mass content (X_{Co}) from the relation as follows:

$$X_{Co} = \frac{\rho_{Co} . V_{Co}}{\rho_{WC} - V_{Co}\left(\rho_{WC} - \rho_{Co}\right)}$$

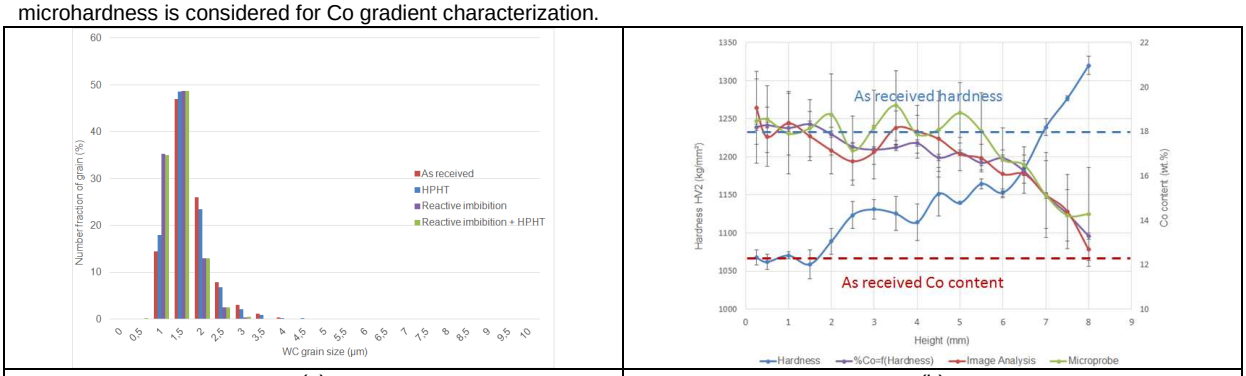
where ρ_{Co} and ρ_{WC} are the density of cobalt phase and tungsten carbide, respectively. In this case, the β-phase (solid solution with a large solubility of W) is assimilated to pure Co.

In the third method, Co content is evaluated using a microprobe (CAMECA-SX100) to make composition profiles along the symmetrical axis of the sample. Measurements are undertaken under 10kV voltage and 80nA intensity. The beam is defocused with a 20µm spot size. For each measurement, five spots around a hardness indentation are used. Contrary to image analysis method, it is directly obtained the Co content in weight percent by microprobe.

An experimental relation between hardness (*HV*) and Co mass content (X_{Co}) obtained by image analysis is established from several samples (as-received, imbibed and HPHT processed samples).

$$X_{Co} = -1{,}82 \times 10^{-5} HV^2 + 2{,}4 \times 10^{-2} HV + 13{,}3$$

where *HV* (kg/mm^2) is the Vickers Hardness (between 1000 and 1600HV) and X_{Co} (wt.%) is Co mass content. These values of cobalt content deduced from microhardness are compared to values measured by image analysis and microprobe experiments. Fig. 3.b compares the results obtained with the three methods. These methods are well correlated, and so the microhardness is considered for Co gradient characterization.



(a) (b)

Fig. 3. WC grain size distribution after each process step (a); Comparison of Co content measured along the revolution axis by three methods from a reactive imbibed substrate (b)

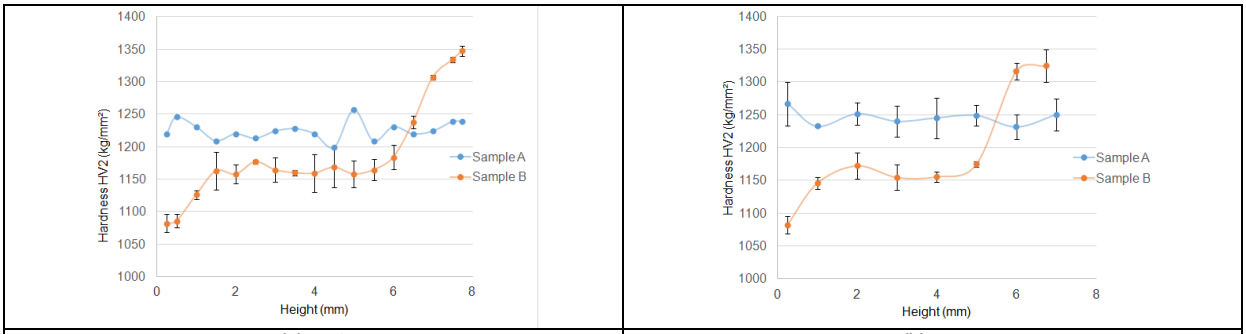
Results

A. Gradient before HPHT

Microhardness measurements are used to quantify the gradients generated by the reactive imbibition process. The microhardness profiles (Fig. 4) are produced along the axis of symmetry (r=0) and the axis oblique (r=z). Fig. 5. show Co distribution for sample A and B along the axis of symmetry. The hardness maps on the right part of the samples are presented in Fig. 6. On the maps, each black spot represents a hardness test mark.

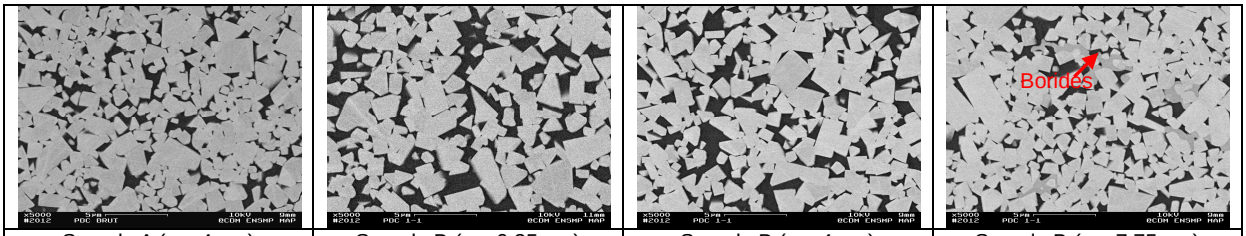
Sample A (as-received substrate) is an unprocessed sample. No significant gradient is present on the hardness maps. The hardness variation is mainly in the range from 1215 to1275HV with an average value around 1245HV.

Sample B is a processed substrate by Reactive Imbibition. On this sample, hardness varies from a minimum of 1080HV in the lower part to a maximum of 1350HV in the upper part. The decrease of hardness in the lower part is undoubtedly due to the migration of the Co-rich liquid phase from the green part. The hardness increase in the upper part is due to the borides formation.



(a) r= 0 (b) r=z

Fig. 4. Microhardness profiles along the axis of symmetry (a); along the oblique axis r=z (b) for as-received (sample A) and reactive imbibed substrates (sample B)



Sample A (z = 4mm)	Sample B (z = 0.25mm)	Sample B (z = 4mm)	Sample B (z = 7.75mm)

Fig. 5. SEM micrographs showing Co distribution in samples A and B on r = 0 axis

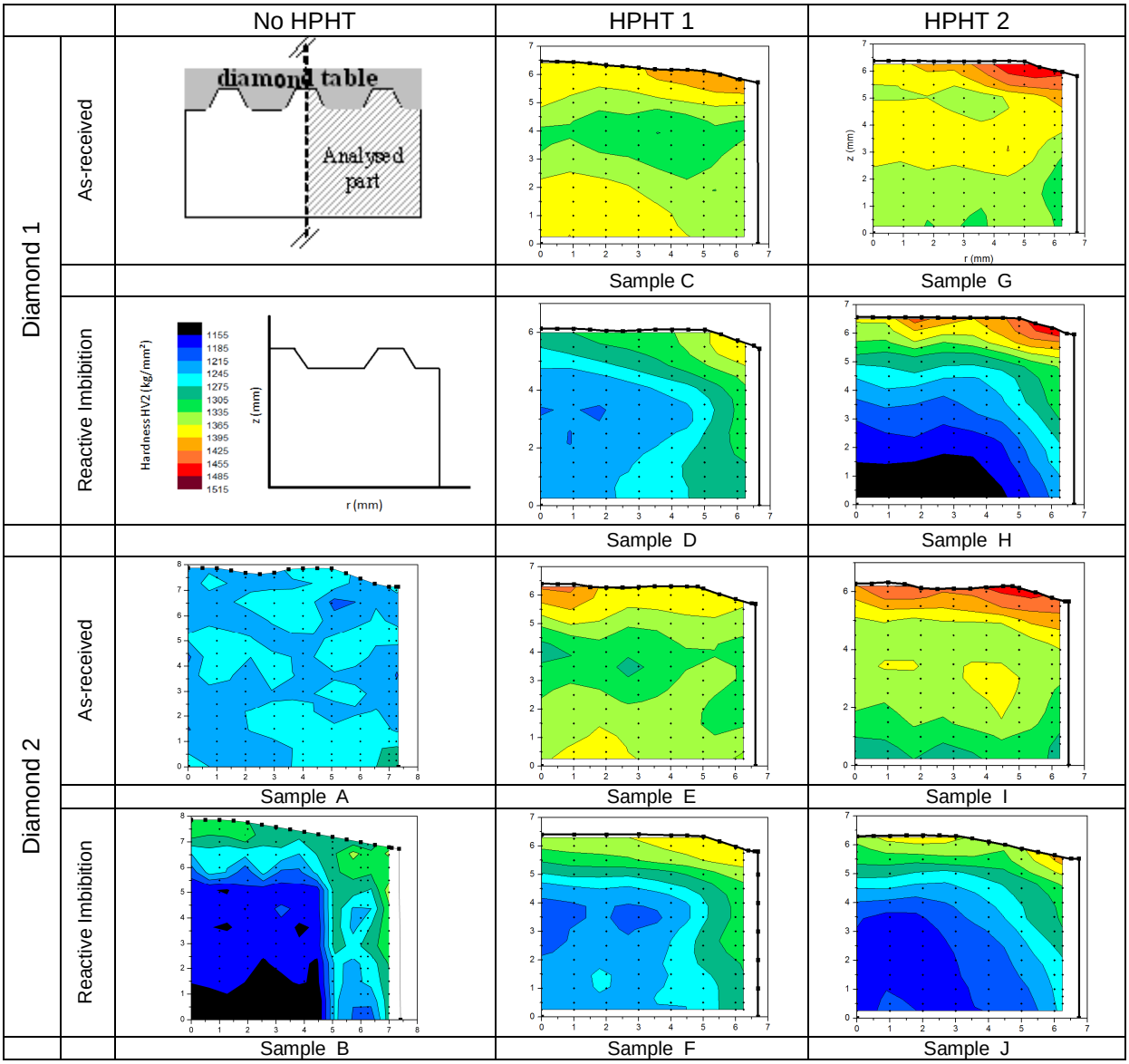


Fig. 6. Microhardness maps

B. Gradient after HPHT: effect of substrate gradation

Whatever the effect studied (substrate gradation, HPHT cycle and diamond grain size), the HPHT process induces a decrease of Co content in the cemented carbide with a hardening of the substrate.

Fig. 6 underlines that the samples C, E, G and I are harder than sample A, in the case of an ungraded substrate. For HPHT processed samples from as-received substrates, the difference of hardness varies from 1275 to 1485HV against 1215 to 1275HV for unprocessed sample by HPHT treatment. So, HPHT process clearly develops a gradation from homogeneous substrates with a amplitude that can reach about 200HV on 6mm-height. These hardness gradients, more particularly, the iso-

values of hardness are parallel to the lower surface.

On the same way, it is observed a similar phenomenon with the graded substrates. The samples D, F, H and J are harder than sample B. In this case, the maximum variation of hardness for HPHT processed samples from a graded substrate ranges from 1160 to 1485HV against 1080 to 1350HV for unprocessed sample by HPHT treatment. The HPHT treatment significantly increases the difference of hardness (ΔHV=325 against ΔHV=270) but it always displays a dome-shaped gradient, generated by reactive coating enriched in boron. This dome-shaped gradient allows associating a hard shell with a softer bulk. The global or mean hardness of these new processed cutters (D, F, H and J) is lower than that of the commercial cutters (C, E, G and I).

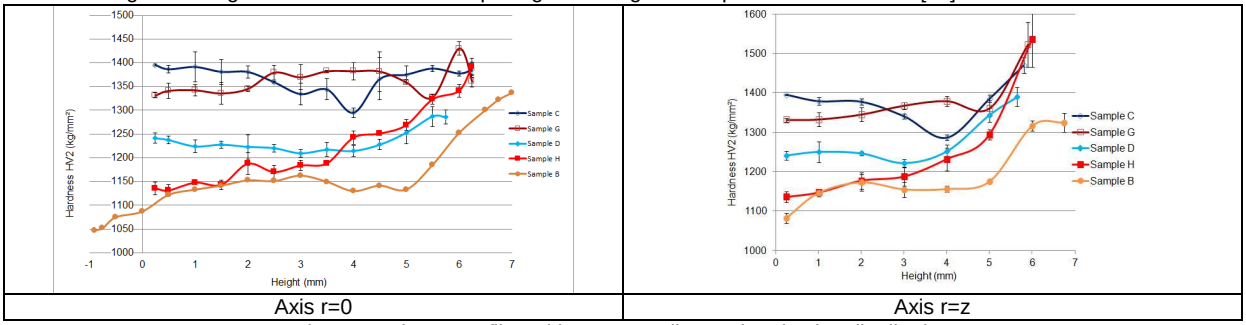
C. Gradient after HPHT: effect of HPHT treatment at “low” and ‘high” Pressure/Temperature

It can be observed the effect of HPHT treatment at "low" and “high” Pressure/Temperature on Fig. 8 and Fig. 9, respectively. A slight decrease of the hardness appears between 3 and 5mm from the bottom of each ungraded substrate (C and E). This phenomenon doesn’t occur for HPHT process at “high” Pressure/Temperature from the same substrate ungraded (G and I).

On graded substrates, the “low” Pressure/Temperature more preserves the dome-shaped gradient and its amplitude is lowered (D and F), compared to “high” Pressure/Temperature (H and J). This difference of hardness can reach about 150HV on 6mm for samples C/E and D/F against about 200HV to 300 HV on 6mm for samples G/I and H/J on the revolution axis. The same statement can be done on the r=z axis. So, for “High” HPHT treatment, the amplitude of gradient can be strongly increased (on an average of 50 to 150HV). All these results support the conclusion established earlier by several authors [19], [20] that the binder phase of the WC-Co substrate migrates, more exactly infiltrates into the diamond compact during the HPHT process in order to act as catalyst for the sintering of diamond powder (neck formation between diamond grains).

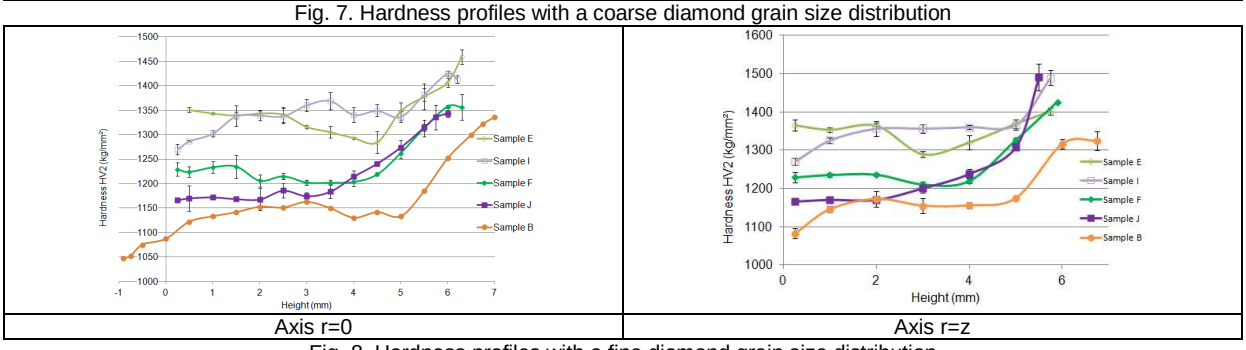
D. Gradient after HPHT: effect of diamond grain size distribution

Fig. 7 and Fig. 8 summarize hardness profiles obtained after HPHT treatment for coarse and fine diamond grain size distributions, respectively. Hardness gradients seem to be very close and then independent of the mean diamond grain size, as shown in Fig. 9 and Fig. 10 These results are surprising and disagree with previous researches [22].



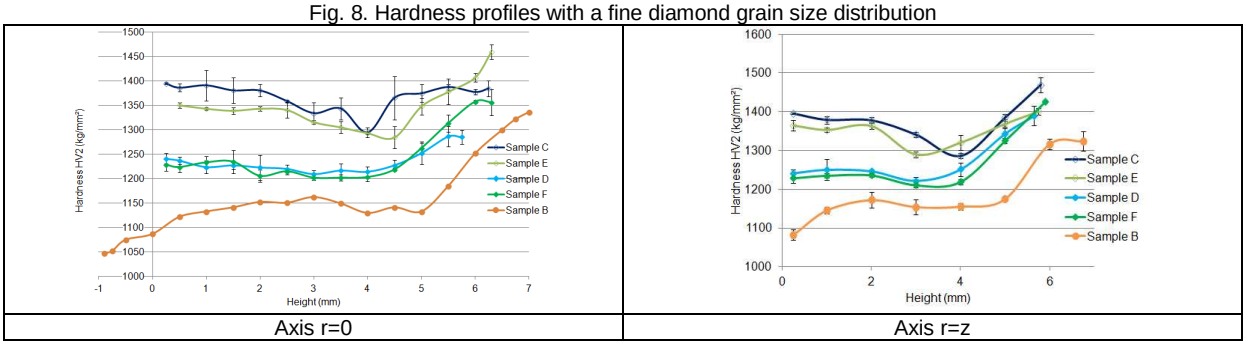
Axis r=0	Axis r=z

Fig. 7. Hardness profiles with a coarse diamond grain size distribution



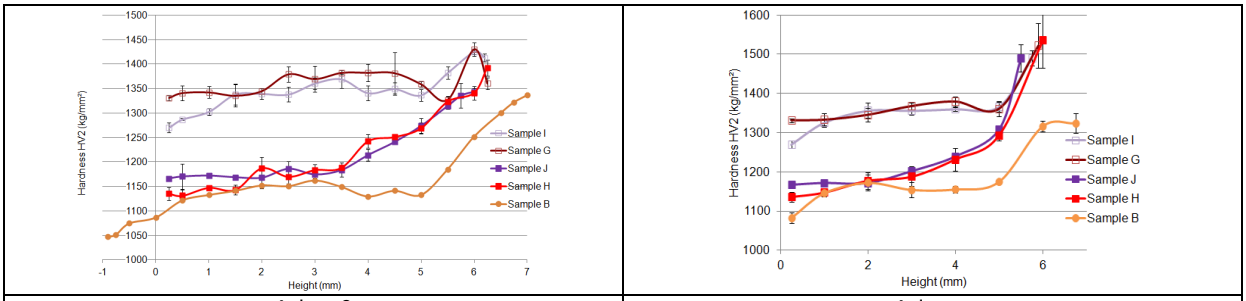
Axis r=0	Axis r=z

Fig. 8. Hardness profiles with a fine diamond grain size distribution



Axis r=0	Axis r=z

Fig. 9. Hardness profiles at "low" Pressure/Temperature for different diamond grain size distributions



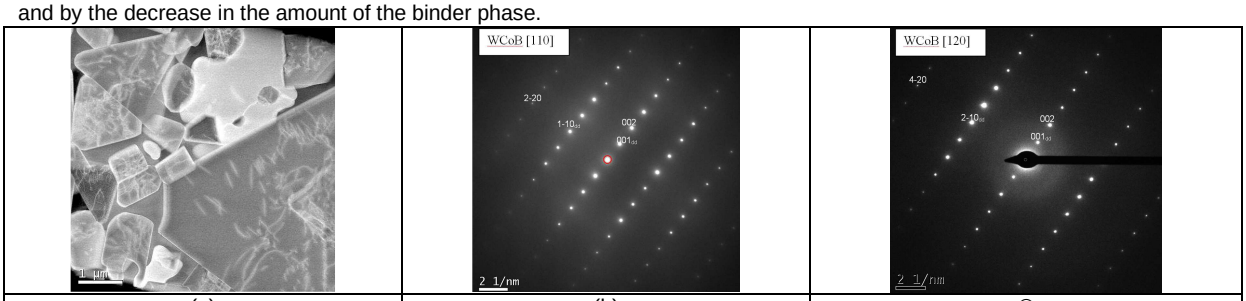
Axis r=0 | Axis r=z

Fig. 10. Hardness profiles at “high” Pressure/Temperature for different diamond grain size distributions

Discussion

The goal of this article was to grade a commercial substrate for PDC cutters in order to improve their shock resistance without reducing their abrasion resistance. Nowadays, it is widely accepted that a component presenting a tough bulk and a hard surface shows superior mechanical properties. The most important gradient obtained in this study reaches 300 HV on 6mm-height, due to a variation of the binder phase into the graded substrate, after HPHT treatment at “high” Pressure/Temperature.

Furthermore, the special shape of the gradient, obtained thanks to the use of the reactive coating, is truly innovative and interesting for mining applications. This particular shape is due to two phenomena before HPHT process: a competition between the liquid migration from the green part and the reaction of the BN coating with the cutter surface, leading to the formation of hardening phases and to a diffusion of the carbon and cobalt towards the bulk i.e. in the opposite direction to liquid migration by imbibition. To confirm the borides formation mechanism proposed by Sorlier [14], some TEM observations were performed in order to validate the presence of the WCoB phase (Fig. 11). This phase is a ternary orthorhombic compound known to enhance the wear resistance of carbide alloys in metal cutting due to its extremely high hardness (about 4300HV).The hardening of the cutter surface under the coating providing the dome shape is thus explained by the formation of a finely dispersed WCoB phase and by the decrease in the amount of the binder phase.



(a) | (b) | ©

Fig. 11. TEM observation of a WCoB phase (lighter phase) in a WC-Co substrate (a), diffraction of the WCoB phase on [110] (b), diffraction of the WCoB phase on [120] (c)

The most interesting result is the conservation or even sometimes improvement of the gradient amplitude after HPHT treatment. This process at high temperature, involves the formation of a liquid phase which could give rise to a complete homogenization of the binder phase into the substrate. In fact, the gradients are modified but preserved after HPHT treatment. According to Sorlier [14], the liquid phase quickly infiltrates by capillarity into the polycrystalline diamond powder compact before sintering takes place. As long as porosity is concerned in powder compact, this infiltration generates a liquid flow under pressure in substrate similar to mass transport during creep tests at high temperatures in cemented carbides [21].

A surprising result is that the initial diamond grain size has no obvious influence on the redistribution of cobalt in the cemented carbides. However, it is widely known that the diamond grain size distribution would have a great influence on the porosity of powder compact before infiltration. Uehara [22] has studied the relation between the volume fraction of cobalt and the initial diamond grain size. The Co content increases in diamond table as the mean diamond grain size decreases. We can assume the different diamond grain size distributions ensure the same porosity in powder compact just before infiltration by liquid phase arising from substrate. This point would be further verified.

Another surprising result comes from the hardness decrease in the center of the ungraded substrate which occurs after a “low” HPHT process. According to the shape of the gradient formed, we can assume that the time at liquid state during “low” HPHT process is longer than “high” HPHT process in order to ensure a good sintering of the diamond table. In this case carbon dissolution from the diamond grains into binder phase would be more important and a carbon gradient takes place into the liquid. Then, a Co migration occurs from the interface towards the lower part of the substrate in the direction of carbon diffusion, as for the DP carbides [3], [4], [5].

Conclusion

Reactive imbibition allows obtaining in one-step a dome-shaped gradient of about 300HV on 6mm without WC grain growth.

After HPHT process, the magnitude of the gradient is preserved and sometimes improved. But the mean hardness of the substrate increases due to the migration of Co phase from the substrate into the diamond compact during the HPHT treatment.

The first mechanical tests show that the service life in abrasion of a graded PDC cutter is improved by 50% in comparison with a standard PDC cutter, tested in the same conditions. Its shock resistance exhibits an increase in performance by 50%.

Acknowledgements

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